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⑤④ Method for bleaching lignocellulose-containing pulp.

⑤⑦ In a method for bleaching lignocellulose-containing pulp with a peroxide-containing compound, the pulp is, prior to the bleaching and in optional order, subjected to acid treatment at a pH of up to about 5 and treated with a complexing agent in order to release transition metal ions from their positions in the pulp. After the acid treatment, a magnesium compound and a calcium compound are added to the pulp at a pH of from about 3.5 to about 8 in order to reintroduce an optimum amount of magnesium and calcium ions into the pulp. The pulp is then bleached with a peroxide-containing compound at a pH of from about 7 to about 13.

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The present invention relates to a method for bleaching lignocellulose-containing pulp with a peroxide-containing compound, in which the pulp, prior to the bleaching and in optional order, is subjected to acid treatment at a pH of up to about 5 and treated with a complexing agent in order to release transition metal ions from their positions in the pulp. After the acid treatment, a magnesium compound and a calcium compound are added to the pulp at a pH of from about 3.5 to about 8 in order to reintroduce an optimum amount of magnesium and calcium ions into the pulp. The pulp is thereafter bleached with a peroxide-containing compound at a pH of from about 7 to about 13.

#### Background of the invention

In the making of lignocellulose-containing pulp of high brightness, the pulp is bleached in one or more stages. For quite some time, mechanical pulp has been bleached with peroxide-containing compounds in alkaline environment, the intention being to remove chromophoric groups but preserve the lignin content. For environmental reasons, it has become increasingly common to treat also chemical pulp as early as in the first bleaching stages with peroxide-containing compounds in alkaline environment, thereby to remove chromophoric groups as well as lignin. Unless the pulp is pretreated, however, such bleaching is less effective than bleaching with chlorine-containing bleaching agents. Thus, hydrogen peroxide bleaching in alkaline environment is disturbed by the presence in the pulp of ions of certain transition metals, primarily Mn, Cu and Fe. These metal ions cause the hydrogen peroxide to disintegrate into undesirable products, thereby reducing the effectiveness of the peroxide bleaching and increasing the consumption of peroxide.

The prior art teaches the bleaching of chemical as well as mechanical pulp with peroxide-containing compounds in alkaline environment and in the presence of magnesium salts. Most of the known bleaching processes do not comprise any acid pretreatment, which preserves the content of desirable as well as undesirable ions in the pulp.

Furthermore, EP-A-0 402 335 discloses the pretreatment of chemical pulp with a complexing agent in order to render more effective subsequent alkaline peroxide bleaching. In this process, it is important that the treatment with a complexing agent takes place at an almost neutral pH. Moreover, this process is not suitable for treating pulp containing large amounts of transition metal ions.

EP-A-0 511 695 discloses acid treatment of a chemical pulp, thereafter adding magnesium and subsequently treating the pulp with alkaline peroxide bleaching.

Therefore, it seems to be obvious to combine the technical features of the prior art and thus to arrive at a process which discloses acid treatment of the pulp, thereafter treating the pulp with a complexing agent and adding magnesium and subsequently treating the pulp with alkaline peroxide bleaching. However, such a process does not improve the brightness of the pulp.

#### Description of the invention

The invention relates to a method in which lignocellulose-containing pulp is treated under the conditions recited in the appended claims, whereby its content of ions having an adverse effect on subsequent alkaline peroxide bleaching is effectively reduced, while at the same time its content of favourable ions is optimised, thereby to obtain a pulp of high strength and brightness with a low consumption of the peroxide-containing compound.

Thus, the invention provides a method for bleaching lignocellulose-containing pulp with a peroxide-containing compound, in which the pulp, prior to the bleaching and in optional order, is subjected to acid treatment at a pH of up to about 5 and treated with a complexing agent, then adding to the pulp, after the acid treatment, a magnesium compound and a calcium compound at a pH of from about 3.5 to about 8 in order to reintroduce magnesium and calcium ions into the pulp, whereupon the pulp is bleached at a pH of from about 7 to about 13.

The initial acid treatment combined with the treatment with a complexing agent in accordance with the invention effectively releases all types of metal ions in lignocellulose-containing pulp. By dewatering or washing the pulp, the thus-released ions can be effectively removed from the pulp suspension. It has therefore been found that the present method effectively reduces the concentration of those ions of transition metals, in particular manganese, copper and iron, that have an adverse effect on the subsequent peroxide bleaching.

In the present method, magnesium ions are reintroduced into the pulp prior to bleaching, thereby increasing the brightness and the strength of the pulp while at the same time reducing the lignin content and the consumption of the bleaching agent. By also reintroducing calcium ions into the pulp, there is achieved a surprising improvement of the final properties of the pulp, especially with respect to brightness.

and reduction of the kappa number. In the present method, it has been found that the content and the positions of magnesium as well as calcium ions have to be optimised to attain the synergistic effect enabling effective peroxide bleaching. Thus, the magnesium and calcium ions have to be added at a pH of from about 3.5 to about 8 in order that the pulp should obtain a sufficient content of these ions.

According to the present invention it is possible to obtain a pulp of high brightness, low lignin content and a on the whole preserved pulp strength while consuming a reduced amount of the peroxide-containing compound. Depending on the type of pulp, inter alia, it is often possible to carry out the method while using a comparatively small amount of complexing agent and a simple washing stage before the peroxide bleaching.

As a result of the acid pretreatment, in combination with the treatment with a complexing agent and the subsequent dewatering or washing stage, essentially all ions are released and removed from the pulp. By the addition of magnesium and calcium, almost all these ions can be reintroduced into the pulp, even under the alkaline conditions prevalent in the peroxide bleaching according to the invention. Thus, the amount of magnesium charged and the amount of magnesium present in the pulp in the peroxide bleaching will be essentially the same. Likewise, the amount of calcium charged and the amount of calcium present in the pulp in the peroxide bleaching will be essentially the same.

The acid treatment and the addition of magnesium and calcium compound are carried out in this order and essentially within different pH ranges. The treatment with the complexing agent may be performed whenever suitable from the point of view of process technique. The treatment with a complexing agent may be carried out in a separate stage before or after the acid treatment or after the addition of magnesium and calcium compounds. Suitably, the treatment with a complexing agent is combined with the acid treatment or the addition of magnesium and calcium compounds. Thus, the acid treatment and the treatment with a complexing agent suitably are performed in a single stage before the magnesium and calcium compounds have been added. However, it is preferred that the treatment with a complexing agent and the addition of magnesium and calcium compounds take place in a single stage after the acid treatment. After the pretreatment into two or more stages, the pulp is suitably dewatered or washed and is then bleached with a peroxide-containing compound at an alkaline pH.

The weight ratio between added Mg and Ca can be from about 1:1 to about 1:4 in order to render effective the alkaline peroxide bleaching. Suitably, the weight ratio of Mg to Ca is from 1:1.2 to 1:3, preferably from 1:1.5 to 1:2.6.

The amount of magnesium compound charged, as well as the amount of calcium compound charged, may be up to about 4000 ppm, calculated as alkaline earth metal by weight of dry pulp. Suitably, the amount of both the magnesium compound and the calcium compound is in the range 100-3000 ppm, preferably in the range of 500-2000 ppm.

The amount of magnesium compound charged, as well as the other conditions, is so chosen that the content of magnesium in the pulp before the peroxide bleaching amounts to at least about 50% of the content of magnesium before carrying out of the present method (the original content). Suitably, the amount of magnesium compound charged, as well as the other conditions, is so chosen that the content of magnesium in the pulp before the peroxide bleaching is in the range of 100-300% of the original content, preferably in the range of 130-200%.

The amount of calcium compound charged, as well as the other conditions, is so chosen that the content of calcium in the pulp before the peroxide bleaching amounts to at least about 25% of the original content. Suitably, the amount of calcium compound charged, as well as the other conditions, is so chosen that the content of calcium in the pulp before the peroxide bleaching is in the range of 50-150% of the original content, preferably in the range of 65-100%.

Suitably, the magnesium-containing compound used is magnesium sulphate, magnesium chloride, magnesium carbonate or magnesium nitrate, preferably magnesium sulphate. Suitably, the calcium-containing compound used is calcium chloride, calcium nitrate, calcium sulphate or calcium carbonate, preferably calcium sulphate. Also compounds containing magnesium and calcium in a suitable ratio may be used, such as dolomite.

In order to achieve a satisfactory effect, the magnesium and calcium compounds should be in dissolved form when brought into contact with the pulp. This can be obtained in various ways, depending on the type and properties of the pulp, among other things. By combining a suitable pH of from about 3.5 to about 8 with suitable temperatures and concentrations of the magnesium and calcium compounds, these compounds can be brought into dissolved form.

Within the scope of the invention, all or some of the magnesium or calcium ions can be added to the pulp suspension via the water used e.g. for pH adjustment or dilution. Thus, hard water containing magnesium or calcium ions, or a combination thereof, may advantageously be used for reintroducing these

ions into the pulp. Examples of such hard water are fresh water from limestone bedrock, white water from paper-making machines using lime or chalk as filler, and process water from sulphite production using magnesium or calcium as base.

The present method preferably comprise a dewatering or washing stage after the treatment with the complexing agent and the addition of magnesium and calcium compounds. As a result, undesirable metal ions can be effectively removed before the peroxide bleaching. The pulp may also be dewatered or washed before and/or after the complexing agent treatment.

By undesirable metal ions are meant not only transition metal ions but also any excess of magnesium and calcium ions. In order that the reintroduced magnesium and calcium ions should not be released from the pulp in another washing stage, the pH in the washing liquid must be at least about 4. Suitably, the pH of the washing liquid is in the range of 5-13, preferably 6-12.

In the present method, the acid treatment is performed at a pH of up to about 5, suitably a pH of from 1.5 to 4, and preferably a pH of from 2 to 3.

In the acid treatment, pH can be adjusted by adding an acid or an acid liquid to the pulp. Use is then made of inorganic mineral acids or residual acid from a chlorine dioxide reactor, either separately or in optional mixture. Suitably, use is made of an inorganic mineral acid, such as sulphuric acid, nitric acid or hydrochloric acid, preferably sulphuric acid.

Manganese ions in the pulp, for example, have an especially adverse effect on alkaline peroxide bleaching. Compounds forming strong complexes with different manganese ions are therefore primarily used as complexing agents. Suitable complexing agents from this point of view are nitrogen-containing organic compounds, primarily nitrogen-containing polycarboxylic acids, nitrogen-containing polyphosphonic acids, and nitrogen-containing polyalcohols. Preferred nitrogen-containing polycarboxylic acids are diethylenetriamine pentaacetic acid (DTPA), ethylenediamine tetraacetic acid (EDTA) and nitrilo-triacetic acid (NTA), DTPA and EDTA being especially preferred. Diethylenetriamine pentaphosphonic acid is a preferred nitrogen-containing polyphosphonic acid. Also other compounds can be used as complexing agents, such as polycarboxylic acids, suitably oxalic acid, citric acid or tartaric acid, or phosphonic acids. Such organic acids as are formed in the treatment of the pulp with chlorine-free bleaching agents, for example, may also be used as complexing agents. The sodium salts of the above complexing agents are preferably used, making the bleach plant a more closed system.

The choice of pH in the treatment with a complexing agent is not critical in the present method, since the magnesium and calcium ions having a favourable effect on the subsequent alkaline peroxide bleaching can be optimised both with respect to amount and position in the pulp. In the present method, the treatment with a complexing agent can thus be performed at a pH of from about 1.5 to about 13. As a result, the treatment with a complexing agent can be combined with the acid treatment, without there being any appreciable reduction of the complexing ability.

The amount of complexing agent charged depends on the type and the amount of transition metal ions present in the incoming pulp, as well as on the effectiveness of the acid treatment and the subsequent dewatering or washing stage. Furthermore, the amount also depends on the type of complexing agent and on the conditions prevailing in the treatment with the agent, such as temperature, residence time, and pH. However, the amount of complexing agent charged can be up to about 5 kg/tonne of dry pulp, based on a 100% product. Suitably, this amount is from 0.05 kg to 2.5 kg/tonne of dry pulp, preferably from 0.1 kg to 1 kg/tonne of dry pulp, based on a 100% product. It is especially preferred that the amount of complexing agent is in the range of 0.2-0.6 kg/tonne of dry pulp, based on a 100% product.

In the present method, the pH in the pulp suspension before the addition of magnesium and calcium compounds is from about 3.5 to about 8, suitably in the range of 4-7.5, and preferably in the range of 4.5-7. It is especially preferred that the pH is in the range of 5-6.5.

Before the acid treatment in the present method, the pulp can be subjected to acid treatment in an additional stage, thereby to obtain a particularly low content of transition metal ions. Such additional treatment may be suitable in alkaline peroxide bleaching of pulp in which the content of transition metal ions is unusually high or in which these ions are difficult to release. One such instance is organosolv pulp.

In a preferred mode of carrying out the present method, the acid treatment is performed in the presence of a delignifying chemical which is effective at a pH of up to about 5. Suitable delignifying chemicals are ozone, acid hydrogen peroxide, per-acids, such as Caro's acid or peracetic acid, and salts thereof, chlorine dioxide and chlorine. Preferably, use is made of ozone, per-acids or salts thereof, or chlorine dioxide, resulting in far-reaching and selective delignification. Ozone and chlorine dioxide are especially preferred.

When chlorine dioxide is used as a delignifying chemical in the present method, it is possible to bleach the pulp to full brightness with an initial chlorine dioxide stage followed by a peroxide stage and still

reducing the produced and discharged amount of chlorine containing compounds to an extremely low level. Thus, the present method optimizes the conditions for an effective peroxide bleaching, whereby a reduced adding of chlorine dioxide can be balanced with an additional, and economically reasonable, adding of peroxide. A reduced adding of chlorine dioxide means that the content of chlorine containing compounds in the pulp, which has been bleached, decreases and the possibilities to close the plants increases essentially. Thus, with the present method, it is possible to decrease the total amount of chlorine containing compounds in the waste water, from all stages, to less than 5 kg/ton pulp, based on the element chlorine. The total amount of chlorine containing compounds in the waste water from all stages will be decreased suitably to less than 3,5 kg/ton pulp and preferably to less than 2 kg/ton pulp, based on elementary chlorine.

When the present method comprises delignification with ozone, the amount may be from about 0.5 kg to about 30 kg/tonne of dry pulp, suitably from 1 kg to 20 kg/tonne of dry pulp, and preferably from 1.5 kg to 10 kg/tonne of dry pulp.

When the present method comprises delignification with chlorine dioxide, the amount can be indicated as a charging factor (CF) as follows

$$CF = \text{total amount of active chlorine in kg/tonne of dry pulp} / \quad (1)$$

kappa number prior to delignification according to the present method.

Thus, 1 kg of chlorine dioxide is equivalent to 2.63 kg of active chlorine. In the present method, the charging factor may be from about 0.1 to about 10, suitably from 0.5 to 5, and preferably from 1 to 3.

The present method can include a dewatering or washing stage after the acid treatment and the treatment with a complexing agent. The pulp may also be dewatered or washed before and/or after the complexing agent treatment. Thus, transition metal ions can be effectively removed prior to the peroxide bleaching. The washing liquid may consist of fresh water, optionally with an addition of a pH-adjusting chemical, or white water from one or more bleaching stages or extraction stages, giving a suitable pH in the washing stage.

In the present method, the acid treatment, treatment with complexing agent and the addition of magnesium and calcium can be carried out at a temperature of from about 10 °C to about 100 °C, suitably from 25 °C to 90 °C, and preferably from 40 °C to 80 °C, and for a time of from about 1 min to about 600 min, suitably from 5 min to 120 min, and preferably from 10 min to 60 min.

The pulp concentration may be from about 1% by weight to about 60% by weight and preferably from 3% by weight to 35% by weight.

The bleaching with a peroxide-containing compound is performed at a pH of from about 7 to about 13, suitably a pH of from 8 to 12, and preferably a pH of from 9 to 11.

The peroxide-containing compound comprises inorganic peroxide compounds, such as hydrogen peroxide, sodium peroxide and peroxy sulphuric acid (Caro's acid), and organic peroxide compounds, such as peracetic acid and performic acid. The peroxide-containing compound suitably consists of hydrogen peroxide or a mixture of hydrogen peroxide and oxygen, and preferably is hydrogen peroxide.

Conventional bleaching conditions can be used.

After the pretreatment stages and the subsequent bleaching with a peroxide-containing compound, the pulp may be used as such for making paper. If so desired, the pulp may also be finally bleached to a higher brightness in one or more stages, e.g. by means of hydrogen peroxide, ozone, sodium dithionite or chlorine dioxide. Final bleaching can also include alkaline extraction stages which may be fortified by peroxide and/or oxygen.

By lignocellulose-containing pulp is meant pulp containing fibres that have been exposed by known chemical or mechanical treatment, or recycled fibres. Suitably, the lignocellulose-containing pulp consists of chemically digested pulp, preferably chemically digested pulp that has been delignified with oxygen prior to the present method. It is especially preferred that the lignocellulose-containing pulp consists of sulphate pulp of softwood.

The invention and its advantages will be further illustrated by the following, non-restricting examples. In the description, the examples and the claims, the figures in per cent and parts are all by weight, unless otherwise stated. Furthermore, the pH values given in the description, the examples and the claims concern the pH at the end of each treatment, unless otherwise stated.

In the examples below, the kappa number, the viscosity and the brightness of the pulp were determined according to the SCAN Standard Methods C 1:77 R, C 15:16:62 and C 11:75:R, respectively. The consumption of hydrogen peroxide and peracetic acid were established by titration with sodium thiosulphate, and potassium permanganate and sodium thiosulphate, respectively.

Example 1: Oxygen-delignified sulphate pulp of softwood having a kappa number of 15.7, a brightness of 37.9% ISO and a viscosity of 990 dm<sup>3</sup>/kg was treated with 15 kg H<sub>2</sub>SO<sub>4</sub>/tonne dry pulp, giving a pH of 2. The acid treatment (A) was performed at 50 °C, a part concentration of 10% by weight and for 30 min. After raising the pH to 5, EDTA (Q), magnesium sulphate (Mg) and calcium sulphate (Ca) were added (test 1). The conditions were so chosen that magnesium and calcium were dissolved in the pulp suspension. The treatment took place at 50 °C, a pulp concentration of 10% by weight and for 60 min. The amount of EDTA added was 2 kg/tonne dry pulp. The amount of magnesium and calcium compounds added was, respectively, 1000 ppm and 1500 ppm, based on alkaline-earth metal per dry pulp. Then, the pulp was bleached with hydrogen peroxide (P) at a temperature of 90 °C, a residence time of 240 min and a pulp concentration of 10% by weight. The addition of hydrogen peroxide was 25 kg/tonne dry pulp, based on 100% hydrogen peroxide, the pH was 10.5-11. After each stage, the pulp was washed with deionised water having a pH of 5.5. Thus, the pulp was first dewatered to a pulp concentration of 25% by weight, and then diluted to a pulp concentration of 3% by weight. After a few minutes, the pulp was dewatered to a pulp concentration of 25% by weight. For comparative purposes, only magnesium sulphate and calcium sulphate (test 2), as well as only magnesium sulphate (test 3) were added after the acid treatment, thereby to illustrate the effect of the complexing agent and of the complexing agent and the calcium ions. The conditions in tests 2 and 3 were otherwise in keeping with those indicated above. The results obtained after the bleaching with hydrogen peroxide appear from the Table below.

TABLE I

Test	Sequence	Pulp properties after H <sub>2</sub> O <sub>2</sub>			Remaining H <sub>2</sub> O <sub>2</sub> kg/tonne
		Kappa number	Viscosity (dm <sup>3</sup> /kg)	Brightness (%ISO)	
1	A-(Q + Mg + Ca)-P	7.1	865	76.4	8.6
2	A-(Mg + Ca)-P	7.3	705	74.9	1.6
3	A-(Mg)-P	8.4	730	71.0	1.6

It is evident from the Table that the pretreatment of pulp in accordance with the present invention results in a strong pulp of high brightness and low lignin content, the consumption of hydrogen peroxide being comparatively low.

Example 2: Oxygen-delignified sulphate pulp of softwood having a kappa number of 8.2, a brightness of 45% ISO and a viscosity of 820 dm<sup>3</sup>/kg was treated in accordance with the present method (test 1). The acid treatment, the addition of EDTA, magnesium sulphate and calcium sulphate in a single stage and the bleaching with hydrogen peroxide were performed as in Example 1. After each stage, the pulp was washed as in Example 1. For comparative purposes, only the complexing agent and the magnesium sulphate (test 2), as well as only the complexing agent (test 3) were added after the acid treatment. The conditions in tests 2 and 3 are otherwise in keeping with those indicated above. The results obtained after the bleaching with hydrogen peroxide appear from the Table below.

TABLE II

Test	Sequence	Pulp properties after H <sub>2</sub> O <sub>2</sub>			Remaining H <sub>2</sub> O <sub>2</sub> kg/tonne
		Kappa number	Viscosity (dm <sup>3</sup> /kg)	Brightness (%ISO)	
1	A-(Q + Mg + Ca)-P	2.2	765	84.9	11.1
2	A-(Q + Mg)-P	2.6	705	81.8	11.0
3	A-(Q)-P	3.4	560	75.0	0

It is evident from the Table that the present treatment of pulp is an environmentally compatible, selective and effective method for bleaching pulp.

Example 3: Oxygen-delignified sulphate pulp of softwood having a kappa number of 14.8, a brightness of 36.4% ISO and a viscosity of 1000 dm<sup>3</sup>/kg was delignified with chlorine dioxide (D), treated with EDTA in

the presence of magnesium and calcium, and bleached with hydrogen peroxide. In delignification, chlorine dioxide was added in an amount equivalent to 30 kg active chlorine/tonne dry pulp, i.e. the batching factor was 2. Delignification was performed at a temperature of 50 °C, a pulp concentration of 10% by weight and for 50 min, pH at the end being 3.9. The addition of EDTA, magnesium sulphate and calcium sulphate in a single stage and the bleaching with hydrogen peroxide were as in Example 1. After each stage, the pulp was washed as in Example 1. For comparative purposes, the pulp was treated without calcium (in test 2), without calcium or magnesium (in test 3) and without complexing agent, calcium or magnesium (in test 4). The results obtained after the bleaching with hydrogen peroxide appear from the Table below.

TABLE III

Test	Sequence	Pulp properties after H <sub>2</sub> O <sub>2</sub>		Remaining H <sub>2</sub> O <sub>2</sub> kg/tonne
		Viscosity (dm <sup>3</sup> /kg)	Brightness (%ISO)	
1	D-(Q + Mg + Ca)-P	850	88.5	11.2
2	D-(Q + Mg)-P	820	85.6	10.7
3	D-Q-P	650	80.1	0
4	D-P	700	77.3	0

It is evident from the Table that a preferred mode of bleaching in which the pulp is delignified with chlorine dioxide results in a strong pulp of very high brightness, the consumption of hydrogen peroxide being comparatively low.

Example 4: The sulphate pulp used in Example 3 was delignified with ozone (Z), treated with EDTA in the presence of magnesium and calcium at different pH values, and bleached with hydrogen peroxide. Delignification with ozone was performed at a pH of 2.1, the temperature of 25 °C, a pulp concentration of about 40% by weight and for 2-3 min. The amount of ozone charged was 7-8 kg/tonne dry pulp. The combined treatment with EDTA and addition of magnesium and calcium sulphate was performed as in Example 1, except that pH was varied. The bleaching with hydrogen peroxide was performed as in Example 1. After each stage, the pulp was washed as in Example 1. The results obtained after the bleaching with hydrogen peroxide appear from the Table below.

TABLE IV

Test	pH	Pulp properties after H <sub>2</sub> O <sub>2</sub>			Remaining H <sub>2</sub> O <sub>2</sub> kg/tonne
		Kappa-number	Viscosity (dm <sup>3</sup> /kg)	Brightness (%ISO)	
1	3.2	3.1	670	83.5	8.4
2	4.1	3.1	745	84.3	12.4
3	5.5	3.0	750	85.1	12.5
4	6.0	3.0	750	85.0	12.2
5	7.2	2.7	705	85.0	9.4
6	9.2	2.9	645	84.9	4.8

It is evident from the Table that the treatment of pulp in the pH range according to the invention results in a pulp of excellent final properties, involving efficient utilisation of the bleaching capacity of the peroxide.

Example 5: The sulphate pulp used in Example 3 was delignified with ozone (Z), treated with magnesium and calcium, and bleached with hydrogen peroxide (P). The complexing agent was added after Z in the same stage as in Mg and Ca (Q2, test 1), as well as before Z (Q1, test 2), in order to illustrate the effect of the point of addition of the complexing agent. Delignification with ozone and the combined treatment with EDTA and addition of magnesium and calcium sulphate were in test 1 performed as in Example 1, as were the bleaching with hydrogen peroxide. In Q1, 15 kg H<sub>2</sub>SO<sub>4</sub> was added per tonne dry pulp, giving a pH of 2.0. Otherwise, Q1 was performed in keeping with Q2, except that the residence time was 30 min. After each stage, the pulp was washed as in Example 1. The results obtained after the bleaching with hydrogen peroxide appear from the Table below.

TABLE V

Test	Sequence	Pulp properties after H <sub>2</sub> O <sub>2</sub>			Remaining H <sub>2</sub> O <sub>2</sub> kg/tonne
		Kappa number	Viscosity (dm <sup>3</sup> /kg)	Brightness (%ISO)	
1	Z-(Q2 + Mg + Ca)-P	3.2	820	82.3	10.8
2	Q1-Z-(Mg + CA)-P	3.1	775	82.9	9.0

It is evident from the Table that a strong and bright pulp is obtained as a result of the addition of the complexing agent, either before or after a delignifying stage in a preferred mode of execution of the present invention.

**Example 6:** Oxygen-delignified sulphate pulp of softwood having a kappa number of 7.7, a brightness of 51.6% ISO and a viscosity of 825 dm<sup>3</sup>/kg was treated with 15 kg H<sub>2</sub>SO<sub>4</sub>/tonne dry pulp, giving a pH of 2.0. The acid treatment was performed at 50 °C for 30 min and with a pulp concentration of 10% by weight. After pH had been raised to 5-5.5, 2 kg EDTA/tonne dry pulp was added together with magnesium sulphate in an amount of 300 ppm, based on magnesium, and calcium sulphate in an amount of 600 ppm, based on calcium. The treatment took place at 50 °C, for 60 min and with a pulp concentration of 10% by weight. Then, the pulp was bleached with hydrogen peroxide at a temperature of 90 °C, for a residence time of 240 min and with a pulp concentration of 10% by weight. The addition of hydrogen peroxide was 25 kg/tonne dry pulp, based on 100% hydrogen peroxide, and pH was 11. After the acid treatment and the peroxide bleaching, the pulp was washed with deionised water having a pH of 5.5. The pulp was first dewatered to a pulp concentration of 25% by weight, and was then diluted to a pulp concentration of 3% by weight. After a few minutes, the pulp was dewatered to a pulp concentration of 25% by weight. For comparative purposes, tests were made involving an addition of but 900 ppm magnesium (Test 2), an addition of but 900 ppm calcium (Test 3), and no addition of either magnesium sulphate or calcium sulphate (Test 4). The results after the hydrogen peroxide bleaching appear from the Table below.

TABLE VI

Test	Mg ppm	Ca ppm	Ratio Mg:Ca	Pulp properties after H <sub>2</sub> O <sub>2</sub>	
				Viscosity (dm <sup>3</sup> /kg)	Brightness (%ISO)
1	300	600	1:2	750	85.0
2	900	0	---	740	82.1
3	0	900	---	670	82.0
4	0	0	---	665	77.4

It is evident from the Table that the combined addition of magnesium and calcium to the pulp results in a strong pulp of high brightness.

**Example 7:** The sulphate pulp used in Example 3 was delignified with chlorine dioxide (D), treated with EDTA in the presence of magnesium and calcium, and bleached with hydrogen peroxide (P), i.e. the sequence D-(Q + Mg + Ca)-P. The pulp was bleached with different combinations of D and P to illustrate the effect of the batching factor on the total amount of the produced chlorine containing compounds at a constant final brightness of 88% ISO. The delignification with chlorine dioxide were as in Example 1, apart from the batching factor which was from 0.67 up to 2. The combined addition of EDTA, magnesium sulphate and calcium sulphate were as in Example 1. The bleaching with hydrogen peroxide were as in Example 1, apart from that the temperature was 105 °C and that the amount of hydrogen peroxide was varied. After each stage, the pulp was washed as in Example 1. The amount of chlorine containing compounds from the sequence was measured in the total volume of waste water. The amounts of chlorate and chloride were measured with ion-chromatography according to the standardized method. The amount AOX was measured according to SCAN-W 9:89. The total amount of the elementary chlorine was measured in each test with titration after reduction with SO<sub>2</sub> at room temperature. As comparison, the same pulp was bleached and delignified to approximately the same brightness as in the sequence D-(EOP)-D-(EP)-D (Test 6). The conditions in each stage were conventional. The



amounts of chlorine dioxide and hydrogen peroxide in test 6 are total in the sequence. The partial pressure of oxygen in the EOP-stage was 0.22. The results obtained after the bleaching with hydrogen peroxide appear from the Table below.

TABELL VII

Test	D as active chlorine (kg/ton)	P (kg/ton)	Brightness (% ISO)	Chlorine compounds in waste water			
				ClO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	AOX	Total counted as Cl
				(kg/ton massa)			
1	10	40	88,1	0,5	1,4	0,20	1,8
2	15	32	88,3	1,1	2,3	0,30	3,1
3	20	26	88,0	1,6	2,9	0,40	4,0
4	25	20	88,4	2,5	3,2	0,53	4,8
5	30	16	88,3	3,1	3,7	0,68	5,7
6	44	4	88,8	4,6	6,4	0,90	8,9

It is evident from the Table that it is possible, with the present treatment of pulp, to produce a pulp with high brightness and at the same time reduce the amount of chlorine containing compounds to a level which permits a highly degree of closing the cellulose factory.

Example 8: Oxygen-delignified sulphate pulp of softwood having a kappa number of 9.6, a brightness of 40.5% ISO and a viscosity of 890 dm<sup>3</sup>/kg was delignified with chlorine dioxide (D) in the presence of EDTA (Q), and bleached with hydrogen peroxide (P) and oxygen (O) in the presence of magnesium and calcium, i.e. in the sequence (D + Q) (P + O + Mg + Ca). The pulp was bleached with various combinations of D and P to illustrate the effect on the batching factor on the total amount chlorine containing compounds produced at a constant final brightness of about 90% ISO. The delignification with chlorine dioxide was performed at a pH of 1.8-2.0, and a temperature of 45 °C for 25 min. The batching factor was varied from 1.0 to 2.5. The added amount of EDTA was 1.5 kg/ton dry pulp. After raising pH to 5-5.5, magnesium sulphate was added in an amount of 300 ppm calculated as magnesium and calcium sulphate was added in an amount of 600 ppm calculated as calcium. Subsequently sodium hydroxide and hydrogen peroxide were added and the pulp concentration was adjusted to 10% by weight. The used autoclave was pressurized with oxygen to 0.22 MPa measured at room temperature. After raising the temperature to 110 °C, the pulp was bleached for 240 min. pH became 11-11.5 after bleaching. After each stage, the pulp was washed as in Example 6. The amount of chlorine containing compounds from the sequence were measured in the total volume of waste water. The amounts of chlorate and chloride were measured with ion-chromatography according to the standardized method. The amount AOX was measured according to SCAN-W 9:89. The total amount of the elementary chlorine was measured in each test through titration after reduction with SO<sub>2</sub> at room temperature. As comparison, the same pulp was bleached and delignified to approximately the same brightness as in the sequence D-(EOP)-D-(EP)-D (Test 5). The conditions in each stage were conventional. The amounts of chlorine dioxide and hydrogen peroxide in test 5 are total in the sequence. The partial pressure of oxygen in the EOP-stage was 0.22. The results obtained after the bleaching with hydrogen peroxide appear from the Table below.

TABELL VIII

Test	D as active chlorine (kg/ton)	P (kg/ton)	Brightness (% ISO)	Chlorine compounds in waste water			
				ClO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	AOX	Total counted as Cl
				(kg/ton massa)			
1	9,6	40	89,8	0,5	1,3	0,17	1,8
2	14,4	30	90,1	1,0	2,2	0,28	2,9
3	19,2	25	90,3	1,5	2,8	0,33	3,8
4	24,0	20	90,5	2,4	3,2	0,50	4,7
5	40,0	3,5	89,9	4,4	4,6	0,85	7,7

It is evident from the Table that it is possible, with the present treatment of pulp, to produce a pulp with high brightness and at the same time reduce the amount of chlorine containing compounds to a level which permits a highly degree of closing the cellulose factory.

#### Claims

1. A method for bleaching lignocellulose-containing pulp with a peroxide-containing compound, characterized by, prior to the bleaching and in optional order, subjecting the pulp to acid treatment at a pH of up to about 5 and treating the pulp with a complexing agent, adding to the pulp, after the acid treatment, a magnesium compound and a calcium compound at a pH of from about 3.5 to about 8 in order to reintroduce magnesium and calcium ions into the pulp, whereupon the pulp is bleached at a pH of from about 7 to about 13.
2. A method as claimed in claim 1, characterized in that the lignocellulose-containing pulp is a chemically digested pulp.
3. A method as claimed in claim 1 or 2, characterized in that the acid treatment takes place at a pH of from 1.5 to 4.
4. A method as claimed in any one of the preceding claims, characterized in that the magnesium and calcium compounds are added at a pH of from 4 to 7.5.
5. A method as claimed in any one of the preceding claims, characterized in that the peroxide-containing compound consists of hydrogen peroxide or a mixture of hydrogen peroxide and oxygen.
6. A method as claimed in any one of the preceding claims, characterized in that the complexing agent is a nitrogen-containing organic compound.
7. A method as claimed in claim 6, characterized in that the nitrogen-containing organic compound is diethylenetriamine pentaacetic acid (DTPA) or ethylenediamine tetraacetic acid (EDTA).
8. A method as claimed in any one of the preceding claims, characterized in that the amount of complexing agent charged is in the range of 0.1-1 kg/tonne of dry pulp, based on a 100% product.
9. A method as claimed in any one of the preceding claims, characterized in that the acid treatment takes place in the presence of a delignifying chemical.
10. A method as claimed in claim 9, characterized in that the delignifying chemical comprises ozone, peracids and salts thereof, and chlorine dioxide.
11. A method as claimed in any one of the preceding claims, characterized in that the acid treatment and the treatment with a complexing agent take place in a single stage.

12. A method as claimed in any one of the preceding claims, characterized in that the treatment with the complexing agent and the addition of the magnesium and calcium compounds take place in single stage.

5 13. A method as claimed in any one of the preceding claims, characterized in that the pulp is dewatered or washed before and/or after the treatment with a complexing agent.

14. A method as claimed in claim 9, characterized in that the delignifying chemical is chlorine dioxide.

10 15. A method as claimed in claim 14, characterized in that the total amount of chlorine containing compounds in the waste water, from all stages, is less than 5 kg/ton pulp, based on the element chlorine.

15 16. A method as claimed in any one of the preceding claims, characterized in that the pulp is dewatered or washed after the addition of the magnesium and calcium compounds.

17. A method as claimed in any one of the preceding claims, characterized in that the pulp is dewatered or washed before the addition of the magnesium and calcium compounds.

20 18. A method as claimed in any one of the preceding claims, characterized in that the weight ratio of Mg to Ca is from about 1:1 to about 1:4.

19. A method as claimed in any one of the preceding claims, characterized in that the pulp is bleached with ozone or chlorine dioxide at a pH of up to about 3.

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